1/1 - (C) FILE CAPLUS
AN - 1980:77480 CAPLUS XP-002214275
DN - 92:77480
TI - Master batch composition for dyeing of a thermoplastic polyester
IN - Tanaka, Yoshiharu; Sakaguchi, Toshiharu; Sakai, Kazufumi; Nara, Ryokich
PA - Tokyo Printing Ink Mfg. Co., Ltd., Japan
SO - Jpn. Kokai Tokkyo Koho, 4 pp.
CODEN: JKXXAF
DT - Patent
LA - Japanese
IC - C08L67/02;C08J3/22
CC - 36-6 (Plastics Manufacture and Processing)
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PN -	JP54129050	A	19791006	JP 1978-36546	19780331 <--

AB - DPDJ 8026 (8:92 Et acrylate-ethylene copolymer) (I) [9010-86-0] or a similar polymer was mixed with copper phthalocyanine blue (II) [147-14 to prep. masterbatches having good dispersibility in poly(ethylene terephthalate) (III) [25038-59-9]. Thus, 45 parts I and 55 parts II w kneaded at 90-110.degree., cooled, cut, pelletized to prep. a masterbat mixed (1 part) with 54 parts III, extruded at 260-70.degree. to prep. a) molding, and melted. No particles having size >2-3 .mu. were obsd.
ST - polyester dyeing compn masterbatch; copper phthalocyanine dye polyester ethylene copolymer dye blend; acrylate copolymer dye blend
IT - Dyeing
(of poly(ethylene terephthalate), masterbatch blends with Et acrylate-ethylene copolymer for improved dispersibility in)
IT - 147-14-8
RL: USES (Uses)
(Et acrylate-ethylene copolymer masterbatch blends with, for dyeing c poly(ethylene terephthalate))
IT - 9010-86-0
RL: USES (Uses)
(copper phthalocyanine blue masterbatch blends with, for dyeing of poly(ethylene terephthalate))
IT - 25038-59-9, uses and miscellaneous
RL: USES (Uses)
(dyeing of, Et acrylate-ethylene copolymer blends with copper phthalocyanine blue for improved dispersibility in)
)

TRANSLATION

JAPANESE PATENT OFFICE
PATENT JOURNAL (A)
KOKAI PATENT APPLICATION NO. SHO 54[1979]-129,050

(51) Int. Cl.[2]	ID Symbol	(52) JPN Cl.	Office Cl. No.	Publication Date: October 6, 1979
C 08 L 67/02		25(1) D 328	7195 – 4J	
3/22			6681 – 4F	

No. of Invention: 1
Examinaiton Request: not filed
(Total of 4 pages)

(54) COLORING MASTER BATCH COMPOSITION FOR THERMOPLASTIC POLYESTER

(21) Patent Application No.: Sho 53[1978]-36,546
(22) Date of Application: Masrch 31, Sho 53[1978]

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SPECIFICATION

1. Title of the Invention

Coloring Master Batch Composition for Thermoplastic Polyester

2. Patent Claims

(1) A coloring master batch composition for thermoplastic polyester characterized by comprising an ethylene-ethyl acrylate copolymeric resin and pigment.

(2) The coloring master batch composition for thermoplastic polyester of Claim 1, wherein the ethylene-ethyl acrylate copolymeric resin has an ethyl acrylate content of 5-30 wt%.

3. Detailed Explanation of the Invention

This invention pertains to a coloring master batch composition for mixing with thermoplastic polyester resins, melting the mixtures and preparing colored moldings.

Because of excellent and balanced characteristics of thermoplastic linear polyester resins such as polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) as a typical example, the resins are widely used in the field of engineering plastics in recent years. However, compared with other resins, it is relatively difficult to prepare colored products of clear coloration of the resins by using a convenient method at a low cost, and consequently, it is difficult to use the resins in decorative products. Therefore, it has been desirable to develop a method to prepare clear-colored moldings at a low cost without damaging the physical properties of polyester.

Previously, there are polyester production processes to add colors to polyester products, but the colors of the products are difficult to change. Therefore, various methods to use coloring master batch compositions (coloring agents), which are prepared by dispersing pigments in a certain kind of carriers and used by adding and mixing at the time of melt-molding of polyester resins, have been proposed. For example, there is a method dispersing a pigment in a polyester resin

dissolved in a solvent, but this method has a difficulty removing the solvent used. Furthermore, there are methods to use glycols and specific dispersants as a carrier and various other proposed methods, but they are all liable to reduce the physical properties due to high hygroscopicity of the carrier used, increase amount of carrier added to moldings because of poor pigment-compatibility, etc. In addition, the use of polyethylene, etc., as a carrier has been considered, but the compatibility of these resins with thermoplastic polyester resins is poor causing a problem of dispersion of the master batch in polyester resins becoming liable to form isle-like lumps (particles having a particle size of several to some 10's of times larger than that of the primary particles of pigment used; consequently, yielding undesirable phenomena based on the dispersion problem of the coloring master batch, for example, uneven coloration problems such as color streak, specks, mottles, etc.; and reducing the product values of those moldings prepared.

The inventors of this invention studied diligently to solve those problems described above, and as a result, they found that various effects described as follows could be achieved if an ethylene-ethyl acrylate copolymeric resin (called EEA, below) was used as a pigment carrier in the coloring master batch.

Specifically, EEA is low-crystalline, shows rubber elasticity, and at the same time, relatively good pigment compatibility because of its slight polarity. Therefore, its viscosity is suitable even if a large amount of pigment, for example, up to about 65% of an organic pigment or about 85% of an inorganic pigment is compounded. This suitable viscosity is utilized for easily pulverizing the raw material pigment in a powder form, which is generally fed in a form of aggregated large particles, by using shearing force of a kneading machine selected from various kinds. As a resin having properties such as good pigment compatibility, suitable softness without using any plasticizer, etc., very similar to those of EEA, there is an ethylene-vinyl acetate copolymeric resin (EVA), but the thermal decomposition of EVA is severe if the processing temperature is over 200°C causing problems such as generating marked formation of acetic acid smell, corrosion of molding mold, etc., reduced physical properties of molding products prepared, etc. In the case of EEA, the thermal stability is high, no thermal decomposition is observed even if the thermoplastic polyester molding temperature in the range of 250-280°C, and the physical properties of moldings prepared are not reduced. In addition, EEA was not known to

have a good compatibility with polyester resins, but surprisingly, as a result of experiments, and pigments in EEA as a carrier were found to be well-dispersible in polyester resins in the form of microparticles. Furthermore, the inventors of this invention also found that if the master batch of this invention was used, no isle-like lump formation was observed at all, and the coloring agent can be uniformly dispersed in moldings prepared in the form of extremely microscopic particles, and they arrived at this invention.

The composition of this invention is a master batch packed with a high content of pigment, thus, the amount of EEA mixed into polyester resins as a carrier is relatively small, and consequently, the consequent reduction in the physical characteristics of moldings is relatively small, and especially it is usable in the case of moldings other than fibers because of hardly any product quality deterioration due to reduced physical properties.

As a thermoplastic polyester resin to be colored by using the coloring master batch composition of this invention, there are linear polyester resins of high degree of polymerization mostly comprising polyalkylene terephthalate such as polyethylene terephthalate, polybutylene terephthalate, polytetramethylene terephthalate, etc., as well as these polyester resins with other polymers and/or third components mixed.

The pigment-carrier, EEA in the coloring master batch of this invention has an ethyl acrylate (EA) content in the range of 5-30%. If the EA content is below 5%, the pigment-compatibility is reduced, and in addition the compatibility with polyester is also reduced causing poor dispersion of the master batch in polyester resins. On the other hand, if the EA content is over 30%, it becomes too soft to achieve proper transmission of shearing force inside the kneading machine, and consequently, it becomes difficult to carry out micro-pulverization of the pigment added.

The pigment used in the coloring master batch of this invention may be any pigment as long as it does not denatured or decomposed by being treated at the melting point of a thermoplastic polyester resin in the colored product, and for example, it can be suitably selected from various commercially available organic or inorganic pigments such as cadmium sulfide, iron ox-

ide, chromium oxide, ultramarine, cobalt-type pigments, carbon black, titanium dioxide, phthalocyanine, quinacridone, naphthol-type pigments, polyazo-type pigments, anthraquinone-type pigments, perylene-type pigments, dioxazine-type pigments, etc.

The coloring master batch of this invention is generally prepared by compounding EEA with a pigment in a weight ratio of 1:0.7 – 1:7, but if the ratio in the range of 1:1 – 1:6 in the case of inorganic pigments or 1:1 – 1:2 in the case of organic pigments is preferable because it is possible to prepare a highly concentrated composition having excellent pigment dispersion.

Incidentally, the master batch composition of this invention may be compounded further with various known additives, for example, various stabilizers such as antioxidant, UV absorber, etc., surfactants, etc.

The raw materials, that is, EEA, pigment, etc., are kneaded in a high-torque kneading machine selected from those known machines with heating devices such as Banbury mixer, biaxial screw-type extruder, double roller kneader, etc., till the crude particles of the pigment added is eliminated, and the maximum particle size is below 2-3 microns. Subsequently, the kneaded mixture is cooled and pulverized to powder or palletized to obtain a coloring master batch composition of this invention.

The coloring master batch composition of this invention is added to a thermoplastic polyester resin so that the amount of pigment is generally in the range of 0.1-3 wt%, and subsequently, auxiliary components such as flame retardant, etc., and filler are mixed, if necessary. The mixture prepared is molded to a desired molding product by using a method selected from various molding methods such as injection molding, extrusion molding, hollow molding, etc.

If the coloring master batch of this invention is used, there are no color unevenness and grit formation because of excellent dispersion of the coloring agent inside colored moldings prepared, the density is improved even if the amount of pigment is small, and it becomes possible to prepare polyester moldings of excellent coloration easily at a low cost. Therefore, the industrial value of this invention is extremely high.

This invention is explained specifically in detail by using application examples and for comparison, reference examples as follows. Incidentally, the part and % in the examples are the part by weight and wt%, respectively.

Application Example 1

A mixture of 45 parts of ethylene-ethyl acrylate copolymer having an ethyl acrylate content of 8% (manufactured by Nippon Unicar Co., trade name DPDJ-8026) and 55 parts of copper phthalocyanine blue was kneaded 3 times by using a double roller kneading machine heated at a temperature in the range of 90-110°C. After cooling to a room temperature by standing, a chip-cutter was used to obtain a coloring master batch in a chip form.

Subsequently, a mixture of 1 part of the coloring master batch prepared and 54 parts of polyethylene terephthalate in its chip form was melt, and an injection molding machine was used to prepare a colored molding having a pigment content of 1% at a cylinder temperature in the range of about 260-270°C. A portion of the molding prepared, about 500 mg was scraped off, melt on a glass slide plate, covered with a cover glass, and the molten solid sample was observed under a microscope with 100X magnification. As a result, the sample showed uniformly colored microparticles being dispersed uniformly and no large particles of the coloring agent larger than 2-3 microns at all.

Application Example 2

The same conditions as those used in the application example 1 were used to prepare a coloring master batch from 40 parts of ethylene-ethyl acrylate copolymer having an ethyl acrylate content of 18% (manufactured by Nippon Unicar Co., trade name DPDJ-6169) and 60 parts of copper phthalocyanine blue.

One part of the coloring master batch prepared and 59 parts of polyethylene terephthalate were used to obtain a molding by using an injection molding machine, and a melt solid sample obtained from the molding prepared was observed under a microscope. As a result, the sample showed uniformly colored microparticles being dispersed uniformly and no large particles of the coloring agent larger than 2-3 microns at all.

Reference Example 1

The same procedures as those used in the application example 1 except that EEA was substituted with 45 parts of ethylene-vinyl acetate copolymer having a vinyl acetate content of 19%. As a result, the smell of acetic acid was generated because of thermal decomposition during injection molding making the workers sick, and the master batch prepared was found to be practically unusable.

Reference Example 2

The same procedures as those used in the application example 1 were carried out to prepare a coloring master batch from 65 parts of low-density polyethylene having a molecular weight of about 20,000 and 35 parts of copper phthalocyanine blue, and a colored PED molding having a pigment content of 1% was prepared. The color density of the molding prepared was apparently lower than those of the moldings prepared in the application examples 1 and 2. In addition, a molten solid sample of the molding prepared observed under a microscope showed extremely poor dispersion of the master batch, 1-3 isle-like lumps per view field of amorphous shapes having a mean diameter of about 10 microns were sporadically present, and in addition, there were also some large particles (grits) of 20 microns or larger particle size.

Applicant: Tokyo Ink K.K.